

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 072 578 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
31.01.2001 Bulletin 2001/05

(51) Int. Cl.⁷: **C07C 29/78**, **C07C 31/26**,
C13F 1/02

(21) Application number: 00115993.8

(22) Date of filing: 26.07.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventor: **Vezzani, Corrado**
20146 Milano (IT)

(74) Representative:
Ferreccio, Rinaldo
c/o Botti & Ferrari S.r.l.
Via Locatelli 5
20135 Milano (IT)

(30) Priority: 30.07.1999 IT MI991721

(71) Applicant:
VOMM CHEMIPHARMA S.r.l.
20089 Rozzano MI (IT)

(54) A method for crystallizing polyols and sugars

(57) A method for the continuous crystallization of
sugars or polyols, comprising the steps of:

- arranging in a thin, turbulent and dynamic layer a continuous flow of melted mass of a compound selected among the group comprising sugars and polyols, with at least 98% of dry material, and a mass of said compound in crystalline form as a crystallization seed;
- advancing said thin layer of material along a cooling wall at a temperature between -15°C and +5°C;
- granulating the material while said thin layer is advanced along the cooling wall, thus obtaining granules of the crystallized compound, and
- cooling said granules to room temperature, after a predetermined maturation time.

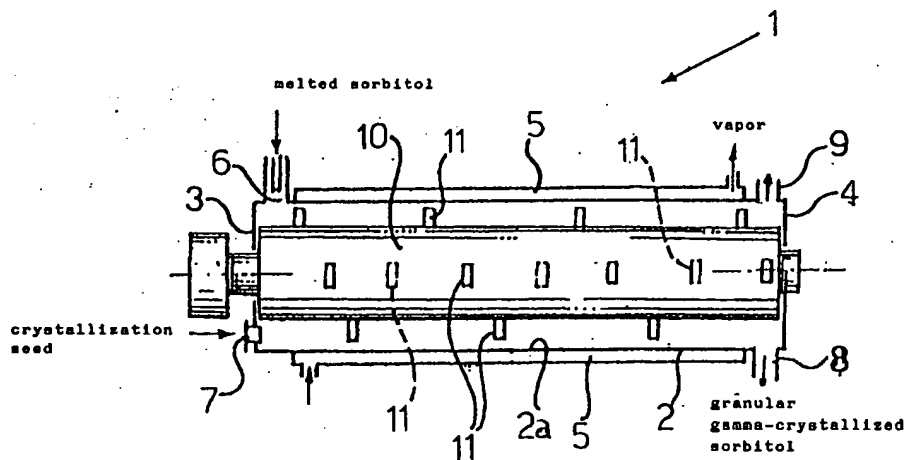


FIG. 1

EP 1 072 578 A1

Description

[0001] The present invention relates to a method for crystallizing sugars and polyols, in particular with reference to sorbitol. The invention also relates to the crystallized sorbitol obtained with such a method.

[0002] The following description mainly concerns a method for the crystallization of sorbitol, since, among all the sugars and polyols compounds, sorbitol is the one which implies the greatest technical difficulties as far as crystallization is concerned.

[0003] Sorbitol has been broadly used as a plasticizer and a filler in many products of the pharmaceutical and confectionery industry, where nowadays is used as a sweetener or as an excipient which "aids" the tableting of the powder formulations containing it.

[0004] Because of its high hygroscopicity, sorbitol must be crystallized at a crystallization degree of at least 80% and must be preferably in the γ (gamma) crystallization form in order to be used in the above mentioned fields.

[0005] As it is known, sorbitol is usually obtained through catalytic hydrogenation of glucose, at the end of which, it is in the form of a highly viscous melted mass (or magma) with a concentration of about 70-72% of the dry material.

[0006] In order to be crystallized in the desired form, the thus obtained sorbitol must be concentrated up to values of 99 + 99,7% of dry material, values at which sorbitol maintains the starting form of melted mass (or magma).

[0007] In order to prepare sorbitol with a high degree of crystallinity, the procedure usually implies cooling the melted and hot sorbitol mass, after adding a suitable quantity of sorbitol crystals or seeds.

[0008] During the cooling, the melted mass of sorbitol is usually kept under constant mixing.

[0009] The crystallized sorbitol is then subjected to fine crushing and to screening.

[0010] Despite the high degree of crystallization, the obtained sorbitol shows the disadvantage of a poor flowability and the tendency to pack when it is subjected to pressure; thus causing problems when the formulations which contain such sorbitol must be tableted.

[0011] According to improved techniques of the above mentioned method, the crystallized sorbitol melted mass is cold extruded and in such a way a higher degree of crystallization and a product more suitable for tableting are obtained.

[0012] But this technique shows an acknowledged control difficulty for a desired uniformity in the treatment of the sorbitol mass and, therefore, gives rise to a non-constant quality in the final product.

[0013] Furthermore, if the extrusion conditions are exasperated or if they are not controlled within a close range of experimentally predetermined values, a vitrification of the product can occur at a certain degree, with a subsequent qualitative decay of such a product and

with a reduction of the already low flowability.

[0014] Another broadly used technique is substantially based on a batch, prolonged treatment, characterized by a slow mixing of the sorbitol melted mass plus crystallized sorbitol added as a seed, in big mixers appropriately equipped (marl treatment).

[0015] Besides the problems related to a batch production, this technique shows the acknowledged inconvenience of the cross contamination. The seriousness and the frequency with which such a contamination occurs make compulsory a thorough cleaning of the mixers at the end of each operative phase, in order to prevent fermentation processes, which would be otherwise inevitable.

[0016] The problem underlying the present invention is that of providing a method for a continuous crystallization of sorbitol, which enables to obtain sorbitol with a high degree of crystallization (or with great amounts of crystallized gamma-sorbitol), overcoming all the disadvantages mentioned with reference to the prior art, and also enabling the crystallization of other polyols and sugars.

[0017] According to the invention, this problem is solved by the method in accordance with claim 1.

[0018] For the steps of formation of the thin layer and of granulation of the material which forms such a layer, an apparatus manufactured by VOMM IMPIANTI E PROCESSI S.R.L. of ROZZANO (Milan) is advantageously used. This apparatus is available on the market with the name TURBOCRYSTALLIZER and includes a cylindrical tubular body, which is closed at its opposite ends by respective end walls and has an inner wall kept at a prefixed temperature by means of a jacket formed in the cylindrical body, a powered rotating shaft, which extends axially in said cylindrical body and is rotatably supported by its opposite end walls, said shaft being provided with radial blades, which are helically arranged and extend nearly up to said inner wall, at least an inlet opening for a flow of material to be treated and at least an outlet opening for the obtained product.

[0019] For the sake of clarity and conciseness, such an apparatus will be named turbocrystallizer in the following description and claims.

[0020] When the above apparatus is used, the method of the present invention comprises the steps described in claims 2-8.

[0021] With particular reference to the production of crystalline sorbitol, the method according to the present invention comprises the steps of

- feeding a first flow comprising melted sorbitol with at least 99% of dry material and a second flow of crystallization seed consisting of crystallized sorbitol, in a turbocrystallizer having the inner wall thermostated at a temperature comprised between -15°C and 5°C, and having a bladed shaft rotating at a speed of 400-1200 r.p.m.;

- intimately mixing said flows, by simultaneously centrifuging them against said thermostated wall, with the formation of a turbulent, tubular, thin layer;
- advancing said thin layer along said thermostated wall with simultaneous and continuous granulation of the mixture of said flows, forming said layer;
- discharging a continuous flow of crystallized granular sorbitol from said turbocrystallizer, and
- cooling to room temperature said granular sorbitol after a prefixed maturation time.

[0022] Advantageously, the above-mentioned flows are fed in the turbocrystallizer in an independent way one from the other.

[0023] The weight ratio between said crystallization seed (crystallized sorbitol) and said melted sorbitol entering the turbocrystallizer, is comprised in the range between 3:1 and 0,5:1 and preferably between 1,5:1 and 1:1.

[0024] The obtained granular sorbitol was shown by analysis to contain more than 95% crystallized gamma-sorbitol.

[0025] This result is surprising if it is considered that the residence time in the turbocrystallizer varies between 20 and 120 seconds and it is mainly due to the basic idea of operating (mixing, crystallizing, granulating) in a thin layer.

[0026] A further and even more surprising result consists in that each sorbitol granule shows an outer surface having a "vitrified" physical aspect, even though it is completely crystallized in the gamma form, as repeated tests have demonstrated.

[0027] This unexpected physical characteristic of the crystallized gamma-sorbitol of the present invention implies a double advantage in comparison with the prior art: a remarkable flowability and a substantial reduction, or even a complete cancellation, of the tendency to pack also when it is subjected to remarkable pressures. All this provides an increased suitability for tableting operations.

[0028] Advantageously, the melted sorbitol is fed in the turbocrystallizer at a temperature comprised in the range 85°C-120°C, while the crystallization seed (crystallized sorbitol) is fed at room temperature.

[0029] The melted sorbitol is preferably obtained directly from the concentration phase of sorbitol produced by catalytic hydrogenation of glucose, while the crystallization seed flow is made by a part of the crystallized gamma-sorbitol, recycled after the maturation step.

[0030] The features and the advantages of the invention will be further clarified by the following description of some exemplary embodiments of the present crystallization method. This description makes reference to the attached drawing provided for illustrative

purposes, in which it is schematically shown a turbocrystallizer of the above-mentioned type.

[0031] In such a drawing, 1 refers overall to a turbocrystallizer comprising a cylindrical tubular body 2, closed at opposite ends by respective end walls 3,4 and provided with a jacket 5. A fluid for thermostating the inner wall 2a of said cylindrical body 2 flows through the jacket 5.

[0032] The cylindrical body 2 is provided at its end wall 3 with two inlet openings 6, 7 for two respective flows of material to be treated, while at the other end wall 4 there is an outlet opening 8 for the obtained product and an opening for discharging any vapors or gases, which are developed during the treatment.

[0033] A motorized bladed shaft 10 axially extends inside the cylindrical body 2 and is rotatably supported by its opposite end walls 3,4.

[0034] There are motor means (not shown) which can rotate said bladed shaft 10 at a speed comprised between 400 and 1200 r.p.m..

[0035] The blades 11 of said shaft 10 extend radially nearly up to the inner wall 2a, of the cylindrical body 2 and are disposed according to a single or a multi-start helicoidal arrangement.

EXAMPLE 1

[0036] A continuous flow of melted sorbitol with a concentration of 99,7% of dry material and at a temperature of 110°C, is fed into the turbocrystallizer 1, whose inner wall 2a is thermostated at +5°C, while the bladed shaft 10 is rotated at a speed of 800 r.p.m..

[0037] A second flow of crystallization seed (crystallized sorbitol) with a ratio 1:1 to the melted sorbitol flow, is continuously fed at room temperature into said turbocrystallizer 1 through the opening 7.

[0038] Immediately upon admission to the tubular body 2, said flows are "taken" by the blades 11, which mix and centrifuge such flows against the inner wall 2a.

[0039] In this condition there occurs the formation of a tubular thin layer of centrifuged material, which is pushed by the blades themselves of the shaft 10, along the inner wall 2a and in heat exchange contact therewith, towards the outlet opening 8.

[0040] During its passage through the cylindrical body 2, the material (melted sorbitol and crystallization seed) of said thin layer is constantly subjected to the mechanical and dynamic action of the blades 11, which besides keeping said material in a high turbulence condition, bring about the granulation (formation and growth of the granule) thereof.

[0041] After an average residence time of 30 seconds, granulated crystallized sorbitol starts to be continuously discharged out of said opening 8 at a temperature of about 55°C.

[0042] The analysis showed that, after a two hours long maturation, the sorbitol granules resulted to be crystallized in the gamma form for more than 95% and

showed a substantially vitreous physical aspect.

[0043] Furthermore, they showed definitely improved taste and solubility in comparison with the prior art.

[0044] Advantageously, the flow of melted sorbitol with 99,7% of dry material entering the turbocrystallizer 1 comes directly from the concentration step of melted sorbitol (concentration: 70% of dry material), which is obtained from the plants for catalytic hydrogenation of glucose.

[0045] Even more advantageously, in order to carry out said concentration step (70% → 99,7% of dry material), it can be used an apparatus which is quite similar to the above-mentioned turbocrystallizer. This apparatus is also manufactured by VOMM IMPIANTI E PROCESSI and it is marketed under the name turboconcentrator.

[0046] In order to obtain the above concentration, the inner wall of the turboconcentrator is thermostated at about 150°C and the bladed shaft is rotated at 400-1200 r.p.m., while the second flow entering said turboconcentrator consists of air at 150°C.

[0047] The crystallized gamma-sorbitol of the present invention is very suitable for tableting and meanwhile can be rolled quite easily.

EXAMPLE 2

[0048] A continuous flow of melted dextrose with a concentration of 98% of dry material and at a temperature of 92°C is fed into the turbocrystallizer 1, whose inner wall 2a is thermostated at +6°C, while the bladed shaft 10 is rotated at a speed of 840 r.p.m..

[0049] A second flow of crystallization seed (crystallized monohydrate dextrose) with a ratio 1:1 to the melted dextrose flow, is continuously fed at room temperature, into said turbocrystallizer 1 through the opening 7.

[0050] After an average residence time of 60 seconds, granulated crystallized dextrose starts to be continuously discharged from said opening 8, at a temperature of about 28°C.

[0051] Also in this case, the flow of melted dextrose with 98% of dry material, entering the turbocrystallizer 1 comes advantageously from the concentration step of a dextrose solution with 70% of dry material, which is available on the market.

[0052] Like in example 1, in said concentration step (70% → 98% of dry material), a turboconcentrator by VOMM IMPIANTI E PROCESSI is advantageously used.

[0053] In the above-mentioned concentration step, the inner wall of the turboconcentrator is thermostated at about 90°C and the bladed shaft is rotated at 750 r.p.m., while the second flow entering said turboconcentrator consists of air at 115°C.

EXAMPLE 3

[0054] A continuous flow of melted fructose with a concentration of 99,1% of dry material and at a temperature of 90°C is fed into the turbocrystallizer 1, whose inner wall 2a is thermostated at +4°C, while the bladed shaft 10 is rotated at a speed of 840 r.p.m..

[0055] A second flow of crystallization seed (crystalline fructose powder) with a ratio 1:4 to the melted fructose flow, is continuously fed at room temperature into said turbocrystallizer 1 through the opening 7.

[0056] After an average residence time of 90 seconds, crystallized fructose starts to be continuously discharged out of said opening 8, at a temperature of about 37°C.

[0057] Also in this case, the flow of melted fructose with 99,1% of dry material, entering the turbocrystallizer 1 comes advantageously from the concentration step of a fructose solution with 70% of dry material, which is available on the market.

[0058] Like in example 1, in said concentration step (70% → 99,1% of dry material), a turboconcentrator by VOMM IMPIANTI E PROCESSI is advantageously used.

[0059] In the above-mentioned concentration step, the inner wall of the turboconcentrator is thermostated at about 160°C and the bladed shaft is rotated at 600 r.p.m., while the second flow entering said turboconcentrator consists of air at 200°C.

Claims

1. A method for the continuous crystallization of sugars or polyols, characterized in that it comprises the subsequent steps of:

- arranging in a thin, turbulent and dynamic layer a continuous flow of material, comprising a melted mass of a compound selected among the group comprising sugars and polyols, with at least 98% of dry material and a corresponding mass of said compound in crystalline form as a crystallization seed;
- advancing said thin layer of material along and in substantial contact with a cooling wall, maintained at a temperature comprised between -15°C and +5°C;
- granulating said material while said thin layer is advanced along the cooling wall, thus obtaining a continuous flow of granules of said crystallized compound, and
- cooling said granules to room temperature, after a predetermined maturation time.

2. A method for the continuous crystallization of sugars

and polyols, characterized by comprising the subsequent steps of:

- feeding a first flow comprising a melted mass of a compound selected among the group comprising sugars and polyols, with at least 98% of dry material and a second flow of crystallization seed consisting of said compound in crystalline form, in a turbocrystallizer having the inner wall thermostated at a temperature comprised between -15°C and 5°C, and having a bladed shaft rotating at a speed of 400-1200 r.p.m.;
 - intimately mixing said flows, by simultaneously centrifuging them against said thermostated wall, with the formation of a turbulent, tubular, thin layer;
 - advancing said thin layer along said thermostated wall with simultaneous and continuous granulation of the mixture of said flows forming said layer;
 - discharging a continuous flow of crystalline granules of said compound from said turbocrystallizer, and
 - cooling to room temperature said granules after a predetermined maturation time.
3. A method according to claim 2, wherein said compound is selected among the group comprising mono- and disaccharides, sorbitol, xylitol and mannitol.
4. A method according to claim 2, characterized in that said first and second flows are fed into said turbocrystallizer independently from one another.
5. A method according to claim 2, characterized in that said second flow of crystallization seed and said first flow of melted compound are in a weight ratio comprised between 3:1 and 0,5:1, preferably between 1,5:1 and 1:1.
6. A method according to claim 2, characterized in that said turbocrystallizer has the inner wall thermostated at a temperature comprised between -15°C and 5°C.
7. A method according to claim 2, characterized in that said bladed shaft is rotated at 400-1200 r.p.m..
8. A method according to claim 2, characterized in that the residence time of the material subjected to treatment in said turbocrystallizer is comprised between 20 and 120 seconds.

9. A method according to claim 1, where said compound is sorbitol, characterized by comprising the subsequent steps of:

- arranging in a thin, turbulent and dynamic layer a continuous flow of material, comprising a melted mass of sorbitol with at least 99% of dry material and a corresponding mass of crystallized sorbitol as a crystallization seed;
- advancing said thin layer of material along and in substantial contact with a cooling wall, maintained at a temperature comprised between -15°C and +5°C;
- granulating said material while said thin layer is advanced along the cooling wall, thus obtaining a continuous flow of granules of crystallized sorbitol, and
- cooling said sorbitol granules to room temperature, after a predetermined maturation time.

10. A method according to claim 3, wherein said compound is sorbitol, characterized by comprising the subsequent steps of:

- feeding a first flow comprising melted sorbitol, with at least 99% of dry material and a second flow of crystallization seed consisting of crystallized sorbitol, in a turbocrystallizer having the inner wall thermostated at a temperature comprised between -15°C and 5°C, and having a bladed shaft rotating at a speed of 400-1200 r.p.m.;
- intimately mixing said flows, by simultaneously centrifuging them against said thermostated wall, with the formation of a turbulent, tubular, thin layer;
- advancing said thin layer along said thermostated wall with simultaneous and continuous granulation of the mixture of said flows forming said layer;
- discharging a continuous flow of crystallized granular sorbitol from said turbocrystallizer, and
- cooling to room temperature said granular sorbitol after a predetermined maturation time.

11. A method according to claim 10, characterized in that said first and second flows are fed into said turbocrystallizer independently from one another.

12. A method according to claim 10, characterized in

that said second flow of crystallization seed and said first flow of melted sorbitol are in a weight ratio comprised between 3:1 and 0,5:1, preferably between 1,5:1 and 1:1.

5

13. A method according to claim 10, characterized in that said turbocrystallizer has the inner wall thermostated at a temperature comprised between -15°C and 5°C.

10

14. A method according to claim 10, characterized in that said bladed shaft is rotated at 400-1200 r.p.m..

15. A method according to claim 10, characterized in that in the residence time of the material subjected to treatment in said turbocrystallizer is comprised between 20 and 120 seconds.

15

16. Granular sorbitol crystallized in the gamma form up to 95% and having a substantially vitreous physical aspect, obtainable by the method of claims 10-15.

20

25

30

35

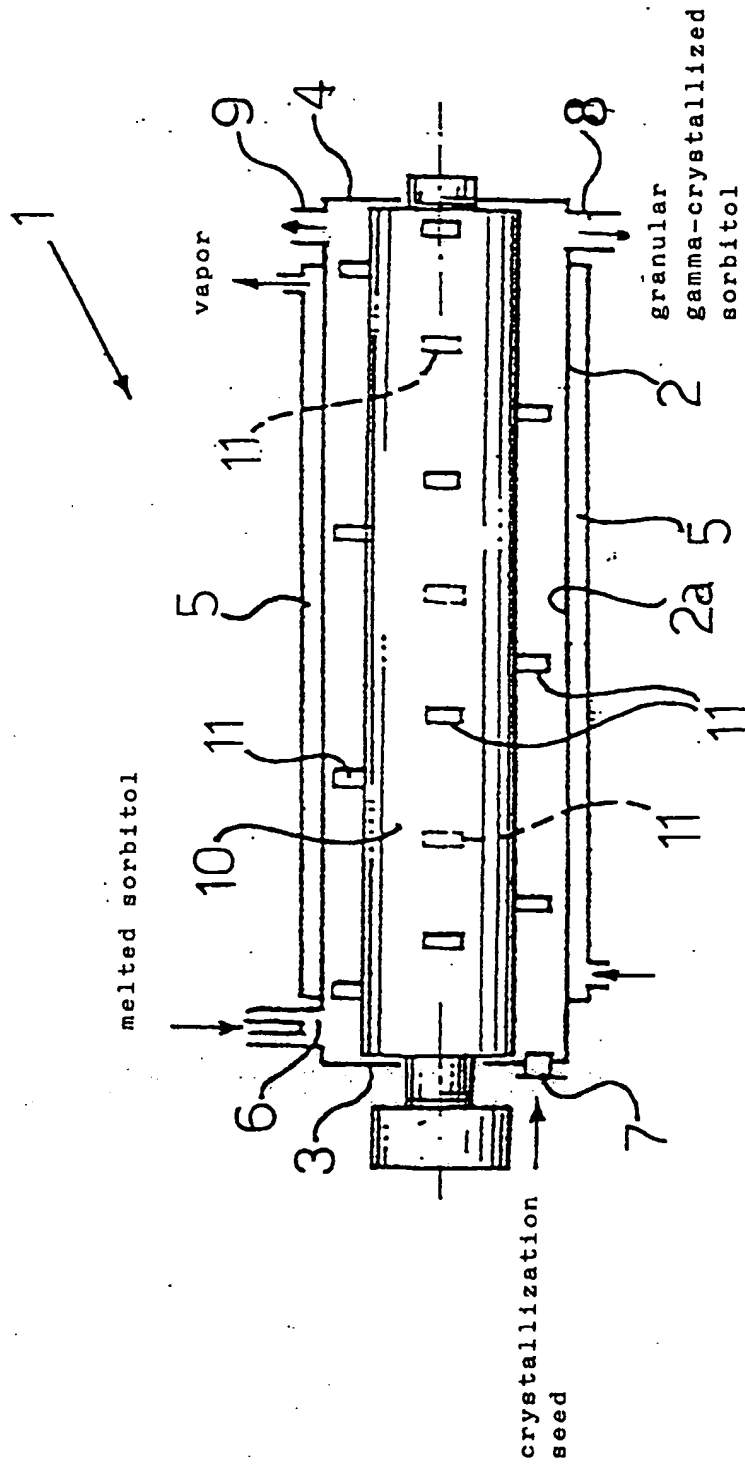
40

45

50

55

FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 5993

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	GB 2 046 743 A (ROQUETTE FRERES) 19 November 1980 (1980-11-19)	1-15	C07C29/78 C07C31/26 C13F1/02
X	* claims 1,2,7; example 1; table 10 * * page 1, line 28-50 *	16	
A	US 3 879 173 A (DE VRIES GERBERTUS H ET AL) 22 April 1975 (1975-04-22) * claim 1; figures 1,4 * * column 1, line 8-45,67 - column 2, line 11,32-55 * * column 3, line 32 - column 4, line 7 * * column 5, line 21-50 * * column 8, line 23-39 *	1-15	
A	GB 1 481 846 A (ROQUETTE FRERES) 3 August 1977 (1977-08-03) * claims 1,9,14; figure 1; example 1 * * page 1, line 60 - page 2, line 52 * * page 4, line 7-56 *	1-16	
X		16	
A	EP 0 542 131 A (VOMM IMPIANTI & PROCESSI SRL) 19 May 1993 (1993-05-19) * claims 1,5; figure 1; examples 1,2 * * column 2, line 51 - column 4, line 10 *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	EP 0 710 670 A (VOMM IMPIANTI & PROCESSI SRL) 8 May 1996 (1996-05-08) * claim 1; figure 1; examples 1,2 * * column 3, line 38 - column 4, line 7 *	1-15	C07C C13F A23L A61K A23G
A	GB 1 287 509 A (TOWA KASEI KOGYO) 31 August 1972 (1972-08-31) * claim 1; examples 1-4 * * page 1, line 73 - page 2, line 85 *	1-16	
-/--			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 November 2000	Examiner Tallgren, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/02 (p04c01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 5993

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 330 352 A (UENO SEIYAKU OYO KENKYUJO KK) 30 August 1989 (1989-08-30) * claims 1,5; examples 1,2 * * page 2, line 44-47 * * page 3, line 12-41 *	1-16	
A	EP 0 885 864 A (MITSUBISHI CHEM CORP) 23 December 1998 (1998-12-23) * claims 2,3; example 1 * * page 3, line 19-22 * * page 4, line 53 - page 5, line 6 * * page 5, line 48 - page 6, line 19 *	1-15	
P,A	EP 1 008 602 A (ROQUETTE FRERES) 14 June 2000 (2000-06-14)	1-15	
P,X	* page 5, line 1-35; claims 6,8; example 1 *	16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 November 2000	Examiner Tallgren, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 11 5993

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-11-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2046743 A	19-11-1980	FR 2451357 A	10-10-1980
		AU 5646580 A	18-09-1980
		BE 882216 A	15-09-1980
		DE 3009875 A	25-09-1980
		DK 110680 A	17-09-1980
		FI 800807 A	17-09-1980
		IT 1149912 B	10-12-1986
		JP 55132628 A	15-10-1980
		NL 8001528 A	18-09-1980
		NO 800748 A	17-09-1980
		SE 8002013 A	17-09-1980
US 3879173 A	22-04-1975	NL 6914626 A	30-03-1971
		BE 752564 A	01-12-1970
		DE 2032909 A	08-07-1971
		OK 130631 B	17-03-1975
		FR 2062847 A	25-06-1971
		GB 1325333 A	01-08-1973
		GB 1326215 A	08-08-1973
		JP 55026883 B	16-07-1980
		SE 382392 B	02-02-1976
		ZA 7005230 A	28-06-1972
GB 1481846 A	03-08-1977	FR 2202867 A	10-05-1974
		BE 818090 A	27-01-1975
		DE 2350619 A	25-04-1974
EP 0542131 A	19-05-1993	IT 1252682 B	23-06-1995
		AT 163902 T	15-03-1998
		BR 9204484 A	18-05-1993
		DE 69224706 D	16-04-1998
		DE 69224706 T	22-10-1998
		US 5409643 A	25-04-1995
EP 0710670 A	08-05-1996	DE 69424942 D	20-07-2000
GB 1287509 A	31-08-1972	JP 52020444 B	03-06-1977
		BE 759609 A	30-04-1971
		CH 520638 A	31-03-1972
		DE 2059246 A	01-07-1971
		FR 2072535 A	24-09-1971
EP 0330352 A	30-08-1989	JP 1213245 A	28-08-1989
		JP 1828511 C	15-03-1994
		JP 5036424 B	31-05-1993
		AU 2983789 A	24-08-1989

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 11 5993

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-11-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0330352 A		CA 1333071 A	15-11-1994
		CN 1035510 A,B	13-09-1989
		DE 68902657 D	08-10-1992
		DE 68902657 T	28-01-1993
		KR 9305255 B	17-06-1993
		US 5068467 A	26-11-1991
EP 0885864 A	23-12-1998	JP 11071310 A	16-03-1999
		US 5981810 A	09-11-1999
EP 1008602 A	14-06-2000	FR 2787110 A	16-06-2000
		BR 9905826 A	08-08-2000
		JP 2000175653 A	27-06-2000

EPO FORM P448

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82